Lithographic Optimization Using Photoresist Contrast

By Chris A. Mack, SEMATECH, Austin, Texas

Optimizing photoresist contrast is one of the oldest and most commonly used techniques for improving a lithographic process. Unfortunately, this method has numerous problems and in many cases yields incorrect results. An example is the use of contrast to optimize a surfactant developer process. The resulting contrast values have little or no relationship to resolution or process latitude. The alternative is to perform linewidth versus focus and exposure experiments as a function of the parameters to be optimized, a time-consuming and expensive process.

This article explores the relationship between photoresist contrast and the properties of a lithographic process which need to be optimized. Using a meaningful definition of contrast, techniques for measuring contrast will be evaluated. The conventional method, resist thickness versus exposure, gives an accurate measure only under certain conditions and fails to consider the dependence of contrast on exposure energy. A more general technique will be given. By understanding the relationship between the measured and actual contrast, the appropriateness of using contrast can be evaluated.

Background

The use of "contrast" to describe the response of a photosensitive material dates back one hundred years when Hurter and Driffield measured the optical density of photographic negative plates as a function of exposure [1]. The "perfect negative" was one which exhibited a linear variation of optical density with the logarithm of exposure. A plot of optical density versus log-exposure showed that a good negative exhibited a "wide period of correct representation", as is shown in the Hurter-Driffield (H-D) curve in Fig. 1. Hurter and Driffield called the slope of this curve in the linear region γ, the "development con-

stant". Negatives with high values of γ were said to be "high contrast" negatives because the photosensitive emulsion quickly changed from low to high optical density when exposed. Of course, high contrast film is not always desirable since it easily saturates.

Photolithography evolved from photographic science and borrowed many of its concepts and terminology. When exposing a photographic plate, the goal is to change the optical density of the material. In lithography, the goal is to remove resist. Thus, an analogous H-D curve for lithography plots resist thickness after development versus log-exposure. The lithographic H-D curve is usually a portion of the complete H-D curve shown in Fig. 1. Because the goal is to completely remove unwanted photoresist, there is usually a range of energies for which all of the photoresist is removed and thus the H-D curve would show no response. If, however, a very thick photoresist and/or a short development time were used so that the resist was not completely removed, the result would be a complete H-D curve. This concept is illustrated in Fig. 2, where the relationship between the lithographic H-D curve of a negative resist and its hypothetical complete curve is shown. It is common practice to normalize the initial resist thickness to one, so that the H-D curve displays the relative thickness remaining.

Following the definition of γ from Hurter and Driffield, the photoresist "contrast" has traditionally been defined as the slope of the lithographic H-D curve at the point where the thickness goes to zero. Thus,
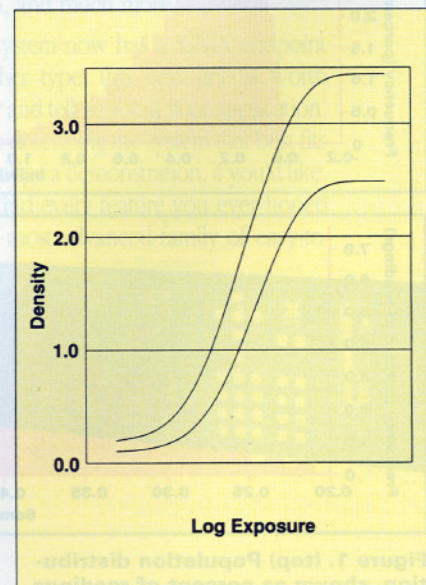
$$\gamma = \pm \frac{1}{T} \frac{d\tau}{d \ln E} \bigg|_{E = E_o} \quad (1)$$

where τ is the resist thickness remaining after development, T is the resist thickness before development, E is the nominal exposure energy, and E_o is the

energy at which τ reaches zero. E_o is called the clearing dose for positive photoresists and the gel dose for negative systems. The positive sign in equation (1) is used for negative resists and the minus sign is used for positive systems in order to keep the value of γ positive. For the remainder of this paper, positive systems will be discussed. The results, however, can easily be applied to negative photoresists as well. (Note that a base-10 logarithm often is used in equation (1) rather than the natural logarithm. This article will always employ the natural log.)

Following the tradition of the photographic sciences, a high contrast photoresist is one which makes a quick transition from being an "under exposed" resist (which does not dissolve) to an "over exposed" resist (which dissolves completely). The traditional definition in equation (1) seems to fit this concept. Furthermore, it is analogous to the pho-

tographic contrast as defined by Hurter and Driffield. The slope of optical density (which is a logarithm of transmittance) versus log-exposure is similar in form to the slope of relative thickness (which is like a log-thickness) versus log-exposure. Thus, it would seem that a suitable definition has been used.

In the last ten years, however, workers in the field of photolithography have found numerous circumstances under which the definition in equation (1) does not meet expectations of what contrast stands for. It is well known that adding a dye to a photoresist decreases the measured value of contrast, usually without reducing exposure latitude [2]. The use of surfactant laden developers dramatically increases measured contrast values [3], although often resolution and exposure latitude are not improved. What causes these apparent discrepancies between the behavior of the measured contrast and our concept of how contrast affects lithography? Is there a problem with the definition or the measurement technique? These questions can be answered by putting the concept of contrast on a firm theoretical foundation and applying rigorous analysis to the observed behavior.

Definition of Photoresist Contrast

With the advantage of retrospect, let us look at the evolution of the traditional definition of contrast and perhaps provide a slightly different definition. In

photography, the desired effect of exposure is a change in the transmittance of the photographic negative. In photolithography, the desired effect is a change in development rate. This change in development rate is manifest as a change in resist thickness after development. Analogous to the photographic H-D curve, let us plot log-development rate versus log-exposure energy. Fig. 3 shows the results for a typical photoresist. Note that this graph gives a complete H-D curve and does not cut off at some energy E_0. We can now state a different definition of contrast, which I shall call the theoretical contrast, γ_{th}:

$$\gamma_{th} \equiv \frac{d \ln R}{d \ln E} \qquad (2)$$

where R is the development rate. (This definition is not very new, dating back at least to Kaplan and Meyerhofer in 1979 [4]. It is also commonly used in electron-beam lithography.) We shall now use this theoretical contrast to quantify the effect of contrast on a lithography process and to compare it to the standard measured value of contrast.

The goal of lithographic exposure is to turn a gradient in exposure energy (an aerial image) into a gradient in development rate. From equation (2), it is very easy to express this effect as [5],

$$\frac{\partial \ln R}{\partial x} = \gamma_{th} \frac{\partial \ln I}{\partial x} \qquad (3)$$

where I is the aerial image intensity and

x is the horizontal distance from the center of the feature being printed. The left hand term is the spatial gradient of development rate. To differentiate between exposed and unexposed areas, it is desirable to have this gradient as large as possible. The right hand side of equation (3) contains the log-slope of the aerial image. This term represents the quality of the aerial image, or alternatively, the amount of information contained in the image about the position of the mask edge. The photoresist contrast "amplifies" the information content of the image and transfers it into the photoresist as a development rate gradient. This expression quite clearly illustrates the role of contrast in defining the "goodness" of a photoresist process.

The theoretical definition of contrast now can be compared to the conventional measured contrast, which now will be called γ_m. The thickness remaining after development for the conventional H-D curve measurement can be described by the following equation:

$$\tau = T - \int_0^{t_{dev}} R\,dt \qquad (4)$$

where t_{dev} is the final development time. Differentiating this equation with respect to log-exposure yields:

$$\frac{d\tau}{d \ln E} = -\int_0^{t_{dev}} \frac{dR}{d \ln E}\,dt \qquad (5)$$

Dividing by the resist thickness and substituting in the definition of γ_{th} gives:

$$\frac{1}{T} \frac{dx}{d \ln E} = -\frac{1}{T} \int_0^{t_{dev}} \gamma_{th} R\,dt \qquad (6)$$

If the development rate is constant from top to bottom of the resist film, the contrast can be taken out of the integral. If equation (6) is evaluated at the energy E_o, the integral becomes one and:

$$-\frac{1}{T}\frac{dx}{d \ln E} = \gamma_m = \gamma_{th}(E_0) = \frac{d \ln R}{d \ln E}\bigg|_{E_o} \qquad (7)$$

Thus, the measured contrast matches the theoretical contrast under the important restriction of constant development rate through the resist film.

To examine what happens when the rate is not constant through the resist film it is convenient to put equation (4) in a different form. An equivalent expression governing the dissolution is [5]:

Figure 2: Conventional photoresist H-D curve for a negative resist with the hypothetical "complete curve" also shown (dashed) for comparison.
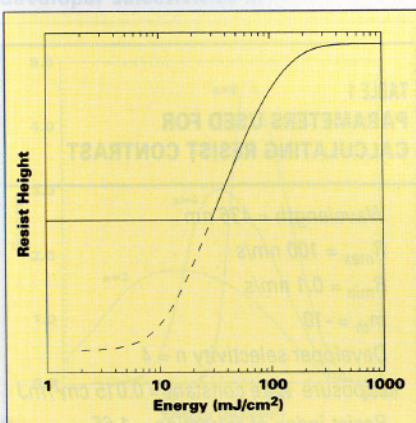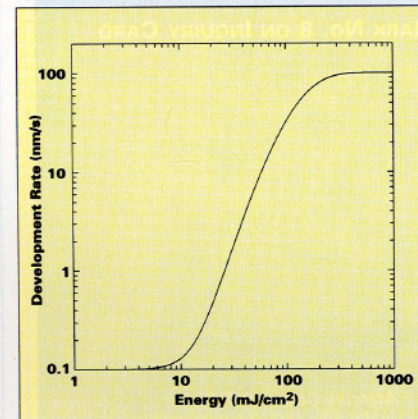
Figure 3: The variation of development rate with energy (plotted in a way analogous to the H-D curve). The slope of this curve is the theoretical contrast.

$$t_{dev} = \int_0^{T-\tau} \frac{dz}{R(z)} \qquad (8)$$

Proceeding as before, we take the derivative of both sides with respect to log-exposure and get:

$$0 = \int_0^{T-\tau} \frac{dR}{d\ln E} \frac{dz}{R^2(z)} - \frac{1}{R(T-\tau)} \frac{d\tau}{d\ln E} \qquad (9)$$

Rearranging:

$$\frac{1}{T} \frac{d\tau}{d\ln E} = -\frac{R(T-\tau)}{T} \int_0^{T-\tau} \frac{d\ln R}{d\ln E} \frac{dz}{R(z)} \qquad (10)$$

Evaluating this expression at $E = E_o$ (i.e., $\tau = 0$) and using the definitions of measured and theoretical contrast:

$$\gamma_m = \frac{R(T)}{T} \int_0^T \gamma_{th} \frac{dz}{R(z)} \qquad (11)$$

If the development rate does not vary through the resist thickness, it is easy to show that equation (11) predicts that measured and theoretical contrast values are equal. Other conditions, such as surface inhibition and resist absorption, can be handled using this equation and will be described in a subsequent section. Equation (11) states that the measured contrast is an average of the theoretical contrast weighted by one over the development rate.

We can now explore the properties of

TABLE 1
PARAMETERS USED FOR CALCULATING RESIST CONTRAST

Wavelength = 436 nm
R_{max} = 100 nm/s
R_{min} = 0.1 nm/s
m_{th} = -10
Developer selectivity n = 4
Exposure Rate constant = 0.015 cm²/mJ
Resist index of refraction = 1.65

the theoretical contrast and in particular its variation with exposure energy.

Exposure Dependence on Resist Contrast

To study the behavior of the theoretical contrast, we will pick the following specific development rate expression which matches experimentally determined development rates for high resolution resists:

$$R = r_{max} (1-m)^n + r_{min} \quad (12)$$

where n is the relative photoactive compound (PAC) concentration and m is a term called the developer selectivity. This equation is a simplification of a previously proposed kinetic model [6] with m_{th} equal to a large negative number. Fig. 3 is a plot of this rate expression with the PAC concentration calculated using standard first order kinetics of the exposure reaction:

$$m = e^{-cE} \quad (13)$$

where c is the exposure rate constant. The values of all parameters used to generate Fig. 3 are shown in Table I. The theoretical contrast can now be derived by differentiating equation (12) with respect to log-exposure, giving:

$$\gamma_{th} = n \left(-\frac{m \ln m}{1-m} \right) \left(1 - \frac{r_{min}}{R} \right) \quad (14)$$

This equation has been derived previ-

ously for the case of $r_{min} = 0$ by applying the development rate expression (12) into the conventional contrast measurement equation (4) and making the assumption of constant development rate through the film [7]. Note that the theoretical contrast is directly proportional to the developer selectivity n. The terms in parentheses give the exposure dependence of γ_{th}. The dependence of contrast on energy is shown in Fig. 4.

Comparing Measured and Theoretical Contrast

We will now use equation (11) to predict the effects of absorption and surface inhibition on the measured contrast. But first, we will describe another method of predicting the measured contrast, using an enhanced version of the PROLITH/2 optical lithography model. Based on the program PROLITH [8], it simulates the exposure and development of positive and negative photoresists with first order exposure kinetics and has the ability to automatically generate standard H-D curves and calculate the measured contrast using the standard definition in equation (1). An example of the output is shown in Fig. 5. PROLITH/2 can now be used as a check against equation (11). The results should be identical under identical conditions. Fig. 6 shows the variation of the measured contrast with exposure energy for the simplest possible case of a non-absorbing photoresist with no surface inhibition on a non-reflecting substrate. In this case, the

measured and theoretical contrasts are the same. One can see that PROLITH/2 and equation (11) give the same results.

The effect of absorption can readily be seen from equation (11). Absorption increases the exposure of the top of the photoresist relative to the bottom. Thus, the development rate at the top of the resist will be greater than at the bottom. The average development through the film will be greater than that at the bottom and equation (11) predicts a measured contrast lower than the theoretical. The results are shown in Fig. 7. As expected, the measured contrast is significantly less when only a moderate amount of absorption is added, even though the theoretical contrast stays the same. Note that the PROLITH/2 simulation has some experimental error associated with determining the slope from a limited number of simulated data points. Increasing the number of points simulated would increase the accuracy of the slope, but the number was left intentionally small to illustrate the difficulty of determining the slope of experimental data. The simulation contained more points than most people would measure in a real experiment, and the accuracy of the thickness values in the simulation is greater. One should expect a fair amount of error in determining the measured contrast from experimental data, even with a high linear regression correlation coefficient. The effect of bleaching on the measured contrast is similar to that of absorption, but the peak contrast shifts to a higher energy.

Figure 4: Energy dependence of the theoretical contrast, γ_{th}, for different developer selectivities n.
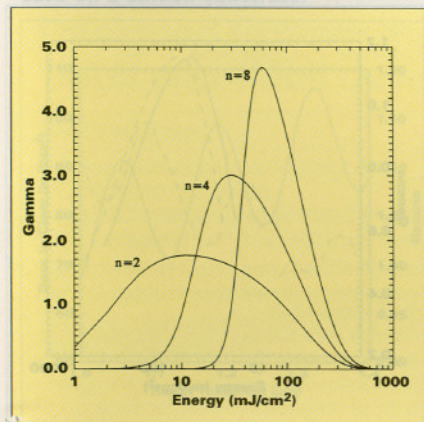
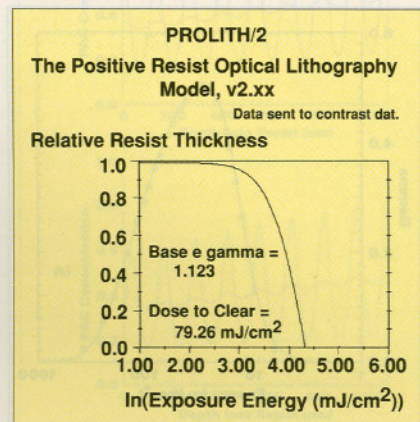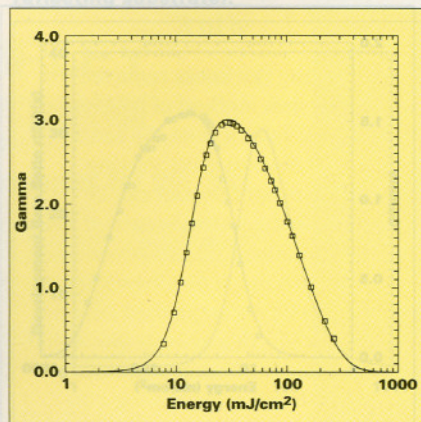**Figure 5: H-D curve as predicted by PROLITH/2.**

Figure 6: Comparison of measured contrast, calculated with equation (11) (solid line) and simulated with PROLITH/2 (squares), for the case of a non-absorbing resist on a non-reflecting substrate.

From equation (11), one can see that the effect of surface inhibition is opposite to that of absorption. A reduced average development rate, relative to that of the bottom of the resist, would result in a measured contrast higher than the theoretical contrast. Fig. 8 shows that, indeed, the measured contrast is much higher than the theoretical contrast when surface inhibition is included. This would explain the observation that arbitrarily high measured contrast values for surfactant laden developers did not translate into improved resolution or process latitude.

Other processes which affect the measured contrast can also be explored, such as reflecting substrates and post-exposure bakes. For these more complicated situations, using PROLITH/2 to predict measured contrast is very convenient. Fig. 9 shows the measured contrast simulated for a silicon substrate with a post-exposure bake for two different resist thicknesses. In this figure, a slight change was made in the method of determining the measured contrast. Rather than using the slope of the H-D curve at zero thickness remaining, a linear regression was performed on the H-D curve between the 10% and 70% thickness points. This method was used in order to facilitate comparison of these results with previously published experimental data, as explained below.

Waldo and Helbert [9] and Luehrmann and Goodwin [10] used contrast in the conventional way as a means of optimizing a photoresist process. One interesting (and to many, unexpected) result was a periodic variation of measured contrast with resist thickness due to thin film interference effects. PROLITH/2 was used to simulate this phenomenon for a particular development time (100 seconds). The results, shown in Fig. 10, show the same behavior as was reported [9,10]. The analysis given in this paper, with a knowledge of the standing wave effect, can be used to explain this behavior and its significance.

As is well known, changing the thickness of a photoresist on a reflecting substrate results in a periodic change in the reflectivity of the film stack due to thin film interference effects. The period of this changing reflectance (in this case 132 nm) is the wavelength divided by twice the index of refraction of the photoresist. This change in reflectivity is, of course, accompanied by a change in the amount of light transmitted into the photoresist. When the resist thickness is such that the reflectance of the stack is at a maximum, the amount of light coupled into the photoresist is at a minimum. Thus, the incident exposure energy must be increased to make up for the reduced coupling in order to get the same effective exposure. This can be seen in Fig. 10 as a periodic change in E_o with resist thickness. It can also be seen in Fig. 9. The two resist thicknesses shown were chosen to be at a minimum and a maximum coupling. The result is a simple shift of the curve to a higher

energy. One might expect that the change in E_o with resist thickness would track the shift in the $\gamma(E)$ curve, resulting in a measured contrast which is independent of resist thickness (except for any bulk effects). Obviously this is not the case. In fact, the measured contrast shows a periodic dependence on resist thickness which is 90° out of phase with respect to the E_o curve. The reason for this strange behavior is far from obvious, but can be explained by understanding the effects of the post-exposure bake on the standing wave pattern.

The standing wave effect causes a sinusoidal variation in the concentration of photoactive compound with depth into the photoresist, $m(z)$. Fig. 11a shows an example of this for a 1.06 μm resist film. Also shown in this figure is the PAC distribution after a post-exposure bake. As expected, the bake simply smooths out the standing wave pattern. Fig. 11b shows the same type of behavior, but for a resist thickness of 1.09 μm. This thickness was chosen to be half way between a maximum and a minimum of energy coupled into the resist. Note that the resist no longer contains an even number of cycles. As a result, the top of the resist contains, on average, a higher concentration of PAC. When the post-exposure bake diffuses out the PAC variation, the top of the resist contains a region of relatively higher PAC concentration. This results in a slower development rate in this top region, creating, in effect, a small surface inhibition effect. This effective surface inhibition due to a

Figure 7: Comparison of measured contrast, calculated with equation (11) (solid line) and simulated with PROLITH/2 (squares), for the case of an absorbing resist (B=0.5 μm⁻¹) on a non-reflecting substrate.
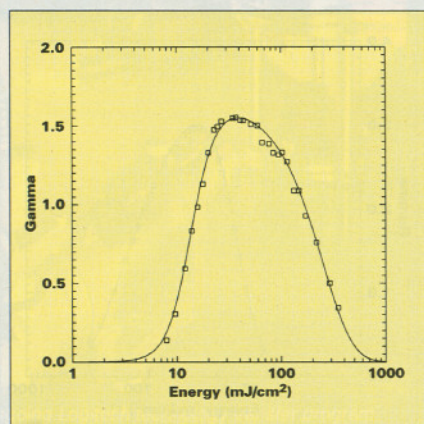

Figure 8: Comparison of measured contrast, calculated with equation (11) (solid line) and simulated with PROLITH/2 (squares), for the case with surface inhibition (relative surface rate = 0.0001, inhibition depth = 0.1 μm).

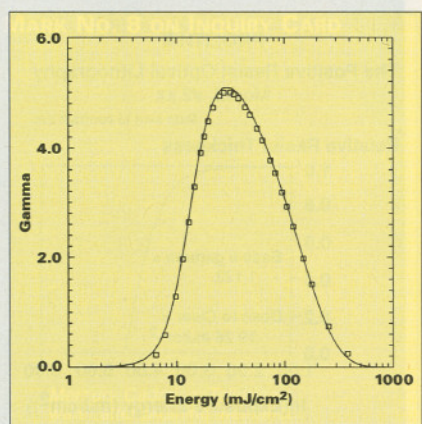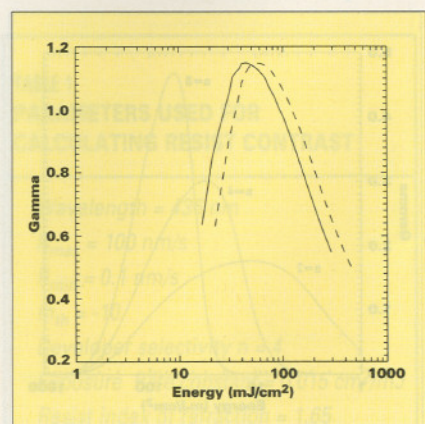Figure 9: Contrast simulated with PROLITH/2 for the case of a bleachable resist (A = 0.6 μm⁻¹, B=0.05 μm⁻¹) on a silicon substrate with a post-exposure bake (diffusion length = 40 nm). Solid line is 1.00 μm thick resist and dashed line is 1.06 μm thick.

locally higher PAC concentration will cause the measured contrast to be higher. As Fig. 10 shows, this is the case for a 1.09 μm thick resist. Similarly, a 1.03 μm resist film will have a locally lower PAC concentration at the top of the film, resulting in an increase in the development at the top of the resist. This in turn will cause the measured contrast to be lower. It is important to note that the theoretical contrast is not affected by the thin film interference effect. The periodic change in measured contrast is nothing more than an artifact of the measurement technique and is another example of how the measured contrast deviates from the theoretical contrast.

Using Contrast to Optimize a Process

The preceding sections have outlined numerous circumstances where the measured contrast deviates significantly from the theoretical contrast. In order to trust the use of contrast to optimize a lithography process, we must answer two questions: (1) how does the theoretical contrast relate to the quality of our process? and (2) can we measure contrast with enough confidence to use the results? In the following section I will suggest alternate measurement methods for contrast which will improve the use of measured contrast. But first, should we even bother with contrast at all?

The justification for using contrast can be found in equation (3). Increasing contrast increases the development gradient in the resist. Equation (3) is only one part of the story, however, being merely a snapshot of what is happening in the development cycle. Let us take the example of finding the optimum exposure energy. Figs. 6-9 clearly show that there is an optimum energy which gives the maximum contrast (call it E_{max}). Should one use this energy as the best nominal exposure dose? Doing so would expose the center of any clear areas at the optimum energy, but the region near the mask edge would get significantly less energy. Typically, the aerial image has an energy of about 30% of the nominal dose at the mask edge. Thus, the line edge would have a contrast far less than the maximum. Should one triple this dose so that the photoresist at the mask edge receives an energy of E_{max}? Doing so would ignore the importance of the development process up to the line edge. The answer is probably somewhere between these two extremes, but looking at contrast alone provides no clue as to the answer.

As an example, the ratio of the development rate at the center of a feature to the rate at the edge of the feature determines the resist profile slope [5]. Fig. 12 shows how this ratio has an optimum energy. In this case the optimum is almost exactly twice E_{max}, the energy which gives the maximum contrast. The variation of contrast with exposure energy is very important, but contrast alone cannot be used to determine the optimum exposure energy.

Optimizing exposure energy is tricky, since the aerial image effectively varies the exposure energy dramatically over a small distance. Can contrast be used for other variables? Any parameter which affects contrast uniformly from the center of the space to the line edge can be optimized using contrast. As a second example, consider the common task of comparing two photoresists using contrast. Suppose resist A is in fact a higher contrast resist (with a selectivity $n = 4$) compared with resist B (with $n = 2$). Since contrast is directly proportional to n, it seems obvious that contrast measurements would point to the better resist. However, closer examination of Fig. 4 shows that this is not necessarily the case. If the energy used for the measurement were too low, resist B would have the higher contrast and appear to be the better resist. This brings out an extremely important point about using contrast to optimize some variable — to be confident of the results, it is necessary to measure contrast as a function of energy.

Measuring Contrast

The above discussion shows the difficulty of using the theoretical contrast as a means of optimizing a lithography process. On top of this, we add the difficulty of being sure our measured contrast accurately reflects the theoretical contrast. It is possible to use equation (11) to extract the theoretical contrast from the measured contrast, but only if
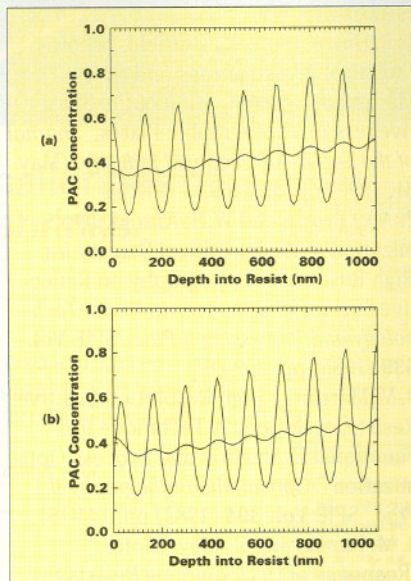
Figure 10: PROLITH/2 simulation of E_o (solid line) and $\gamma m (E_o)$ (dashed line) as a function of resist thickness for exposure on a silicon substrate.

Figure 11: PAC concentration before and after a post-exposure bake for (a) 1.06 μm thick resist, and (b) 1.09 μm thick resist.
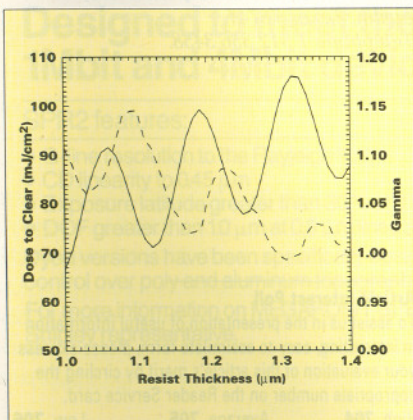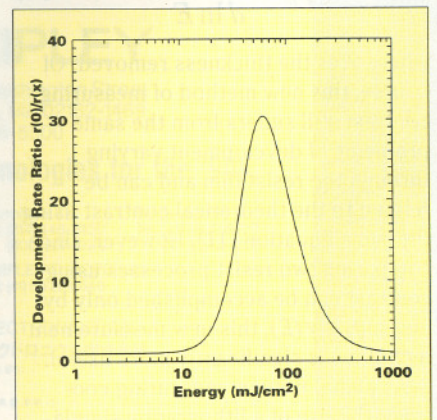
Figure 12: Using the ratio of center-to-edge development rates to find the optimum exposure energy (for the case of a non-absorbing resist on a non-reflecting substrate).

the variation of development rate through the film is known. In some simple cases, such as absorption in the resist, this may be possible. The most critical problem is the presence of surface inhibition. Even a small amount of surface inhibition can make the resulting measured contrast totally useless. Therefore, any parameter which changes the amount of surface inhibition cannot be optimized using measured contrast. Is there a better way to measure contrast?

The ideal method of determining γ_{th} (E) is with a development rate monitor (DRM). A DRM can measure $R(E,z)$ directly allowing calculation of the theoretical contrast from its definition, equation (2). One must still remember that the value of E used is the actual energy deposited in the film at position z, not the incident energy. Using a DRM significantly complicates the process of measuring contrast. It is, however, the only foolproof method.

It is possible to improve on the conventional measurement technique for contrast using our definition of theoretical contrast as a guide. We desire an approximate method of measuring development rate without using a DRM. Rather than using the thickness remaining after development, let us use the thickness *removed* after development, which is proportional to the development rate. Since the true contrast is determined by plotting log-development rate versus log-exposure, we will plot log-thickness removed versus log-exposure. Finally, in order to obtain as close to a complete H-D curve as possible, we will make our development time used in the measurement as short as possible. The resulting data allows us to determine measured contrast as a function of energy, rather than at one energy E_0. The new measured contrast is defined as:

$$\gamma_m = \frac{d \ln \tau_r}{d \ln E} \quad (15)$$

where γ_r is the thickness removed. Of course, this new method of measuring contrast still suffers from the same problems of development varying through the resist film and can be related to the theoretical contrast using the same equation (11). However, since comparing two resist processes using contrast can be accomplished only by measuring $\gamma(E)$, this new measurement technique is significantly more useful.

As a final note on measuring contrast, the use of a lithography simulation tool can be an extremely valuable aid. The model can be used to predict the log-thickness removed versus log-exposure curve. The values of the development rate parameters used in the model, in particular the developer selectivity n, can be adjusted to get the best fit to experimental data. It is the value of n which can provide useful comparisons of different photoresist processes.

Conclusions

The use of measured contrast to optimize a photoresist process is fraught with pitfalls. As the preceding analysis has shown, the measured contrast can deviate significantly from the true contrast. However, equation (11) for the first time gives us a tool which can help us understand these deviations and, in some cases, correct for them. Furthermore, an enhanced measurement method has been proposed which provides information about the energy dependency of the contrast. The careful application of the enhanced measurement method with the understanding of equation (11) can, in some circumstances, lead to an accurate determination of the true contrast.

Once the contrast has been determined, care must be used in applying this information to optimize a resist process. It is *essential* to measure contrast as a function of energy and compare the entire curves to determine if one process is better than another. Finally, although the variation of contrast with exposure is extremely important, it cannot be used to optimize exposure energy.

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Chris A. Mack received Bachelor of Science degrees in Physics, Chemistry, Electrical Engineering, and Chemical Engineering from Rose-Hulman Institute of Technology in 1982, and a Master of Science degree in Electrical Engineering from the University of Maryland in 1989. He joined the Microelectronics Research Laboratory of the Department of Defense in 1983 and began his work in optical lithography research. He has authored numerous papers in the area of optical lithography, regularly teaches courses on this topic, and has developed the lithography simulation programs PROLITH and PROLITH/2. He is currently on assignment at SEMATECH.